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REFRACTORY MATERIALS FOR THE GLASS INDUSTRY

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FORMATION OF THE PHASE COMPOSITION OF UNSINTERED REFRACTORY CONCRETES IN THE OPERATING TEMPERATURE RANGE OF GLASSMAKING EQUIPMENT

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Comprehensive studies of the phase composition of refractory concrete compositions heat-treated in different temperature intervals, including the operating range of glassmaking equipment, have been performed. The characteristic changes of the phase composition of unsintered concretes during the transformative heat-treatment have been established; a new phase appears after sintering at 1000°C — calcium aluminosilicate $2CaO \cdot Al_2O_3 \cdot SiO_2$, which attests to the interaction in the sample of calcium aluminates with free silica — microsilica or aluminosilicates.

Key words: refractory low-cement concrete, matrix, high-dispersity silica (microsilica), phase composition, operating properties, glassmaking furnace.

The production and use of advanced refractory concrete materials in the form of dry mixtures as well as the ready elements of linings have been continually increasing in the last few decades. The Semiluki Refractory Works is developing refractory low-cement concretes for use in production equipment used in the glass industry [1, 2].

Concrete as a composite material consists of two main parts — a filler with particles ranging in size from several mm to 45 μm and a binder or matrix. The matrix of low-cement concrete contains a fine fraction of filler, cement, and finely dispersed components with particles less than 10 μm as well as additives which regulate the technological properties of concrete. In composite dispersion-hardened materials the matrix is the main element determining its strength and refractory properties [3]. High material strength is attained with particle size in the range 10 – 500 nm with average interparticle separation 100 – 500 nm and uniform particle distribution in the matrix.

One component of the matrix of a refractory low-cement concrete is microsilica — high-dispersion silica with average particle size 150 nm (Fig. 1). Since the particles are so small, the microsilica possesses high reactivity and even at room temperature it forms a gel on interacting with water. Its use in concretes makes it possible to decrease the water needed in a concrete mixture and lower the content of cement while maintaining strength. Having high specific surface area (15 – 25 m^2/g) microsilica even in small amounts plays a large role in the formation of the phase composition and structure of the material [4].

The most important technological factor for phase-formation processes is the article sintering temperature: in refractory concretes which are not sintered at high temperature the structure and phase composition are formed when the equipment reaches its operating regime and then during service of the refractories.

The objective of the present work was to determine by x-ray phase analysis [5] the mechanisms of the formation of the phase composition of aluminosilicate low-cement refractory concretes (manufactured by Semiluki Refractory Works, JSC) in the temperature interval 110 – 1400°C in order to determine the range of their best use in the elements of the lining of the thermal equipment. Samples of fireclay concrete materials and matrices (binders) heat-treated successively at 110 and 380°C and then sintered at 1000 and 1400°C were used for these investigations.

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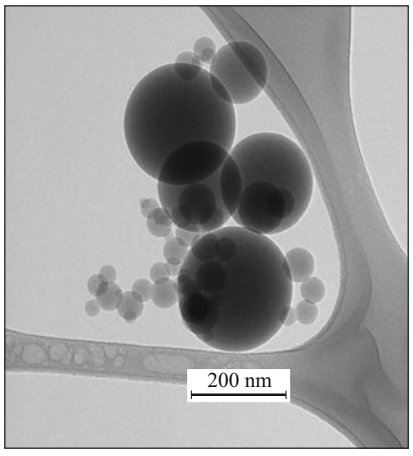

Fig. 1. Photograph of particles of highly dispersed silica (microsilica).

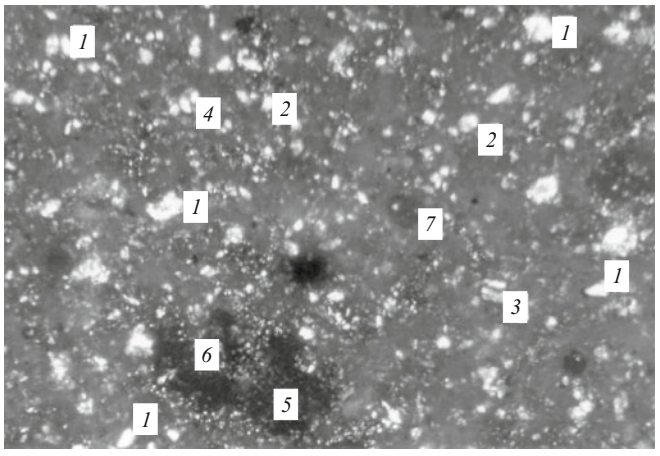

Fig. 2. VShS-1 binder; treatment temperature 380°C. Cristobalite manifest weak isotropy: *1*) calcium aluminates; *2*) calcium silicates; *3*) cyanite; *4*) sillimanite; *5*) pores; *6*) cryptocrystalline structure of cristobalite; *7*) ferruginous glass phase; polaroids +; × 150.

The diffraction patterns of the samples were recorded with a Huber G670IP focusing Guinier camera ("in transmission," $CuK\alpha_1$ radiation, Johanson-bent $SiO_2(101)$ monochromator, Imaging-Plate detector). To perform the experiment a sample was ground in an agate mortar and mixed with an x-ray amorphous binder — nitrocellulose varnish (solution of nitrocellulose in isoamyl acetate), after which a thin layer of the suspension was placed on an x-ray amorphous lavsan film. The results were analyzed with the STOE WinXPow program package and the ICDD PDF-2 database was used for high-quality phase analysis.

Comparing the profile of the diffraction patterns of binders heat-treated at different temperatures showed that the samples heat-treated at 110 and 380°C are practically identical. Negligible changes occur after heat-treatment at 1000°C (actually, the appearance of a single new reflection near 31.8°2θ). After heat-treatment at 1400°C a substantial number of reflections vanish with new ones appearing, which attests to the occurrence of a series of reactions.

After the initial heat-treatment at 110 and 380°C, corundum Al_2O_3, α-quartz SiO_2, cristobalite SiO_2, and aluminum silicates — the compound Al_2O_3 with SiO_2 with variable composition and cyanite $Al_2O_3 \cdot SiO_2$, as well as calcium aluminates grossite $CaO \cdot 2Al_2O_3$ and $CaO \cdot Al_2O_3$ — are present in the binder samples. Petrographic studies confirm these data [6].

When the temperature is increased to 1000°C, a new phase appears in the binder — calcium aluminum silicate gehlenite $2CaO \cdot Al_2O_3 \cdot SiO_2$ — attesting to an interaction of calcium aluminates with microsilica in the sample. This is also confirmed by a rapid decrease (to vanishing) of the area of the halo, corresponding to an amorphous glass phase (18 – 20°2θ), in all other samples.

Petrographic studies showed that after an article is heat-treated at 380°C (Fig. 2) aluminum silicates $CaO \cdot 2Al_2O_3$ and $CaO \cdot Al_2O_3$ appear in the binding substance. Individual oxides were found in the samples: corundum Al_2O_3, α-quartz SiO_2, cristobalite SiO_2; aluminosilicates: mullite with nonstoichiometric composition and cyanite $Al_2O_3 \cdot SiO_2$. A further increase of the heat-treatment temperature results in growth of calcium aluminate and aluminosilicate crystals as compared with a sample of the same material but heat-treated to 380°C. Cryptocrystalline cristobalite and a glassy phase, finely dispersed mullite and aluminosilicates are determined in thin sections of a metallographic specimen.

The property of forming a glass phase and aluminosilicates at low temperatures is a distinguishing feature of concrete technology — a gel forms already at the first stages of the solidification of the cement. Microsilica plays an important role in the mechanism of the interaction of active microfillers of the binder with the hydrating minerals of cement. Calcium hydroaluminosilicates form; they are distinguished by a developed spatial structure and permit denser filling of the pores in the concrete structure which is forming. The start of the mullite-formation reaction at such a low temperature (380°C) is also a result of the high reactivity of microsilica.

The diffraction patterns of a sample sintered at 1400°C show that softening/vitrification of the amorphous phases occur.

Calcium aluminate and silicate crystals are rarely encountered in photomicrographs of the binder, probably because they dissolve during sintering, but they are seen as replicas with a bright interference coloring which have converted into aluminosilicates. Increasing the temperature initiates growth of mullite fibers (Fig. 3). Quartz and calcium aluminates are virtually absent in the material, being present in amounts much less than cristobalite, though a new phase appears in large quantities — calcium aluminosilicate anortite $CaO \cdot Al_2O_3 \cdot 2SiO_2$. This attests to a strong interac-

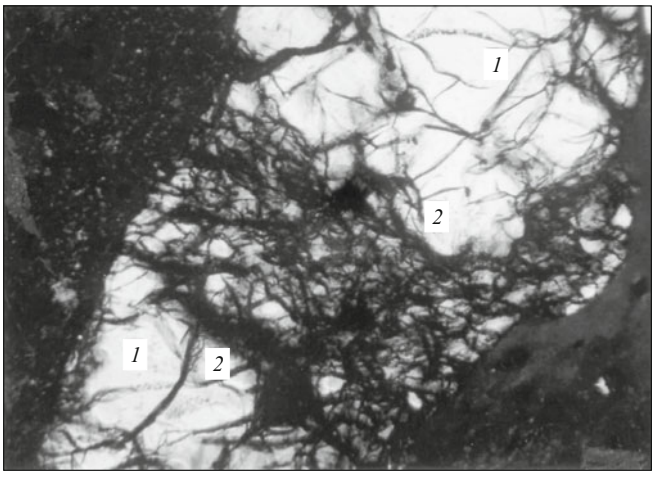

Fig. 3. VShS concrete, sintering temperature 1400°C. Substitution of large cyanite (*1*) crystals by mullite fibers (*2*); polaroids +; × 150.

tion between free silica and calcium aluminate with the aluminosilicate phases being practically inert.

As the sintering temperature increases to 1400°C, the maximum absolute intensity of the signals increases systematically; this corresponds to improvement of the crystallinity of the samples with increasing temperature.

Generalizing the results described in [6, 7] and obtained in the present investigation, it can be stated that as a result of heat treatment of the fireclay cement samples at 110°C a structure characteristic of concrete is observed — an amorphous gel-like phase is detected. The binder of the material is based on an aluminosilicate phase and an alumina phase, an almost isotropic substance; in addition, calcium hydroaluminates are determined in the interior volume of the particles.

Heat treatment of the samples at 380°C results in the appearance of calcium aluminates in the binder; cyanite and mullite aluminosilicates with nonstoichiometric composition are present in the sample together with the oxides Al_2O_3 and SiO_2.

As the heat treatment temperature is increased to 1000°C, the binder penetrates into the fireclay along the contour and activates the formation of mullite crystals, an increase of the size of calcium aluminate crystals is observed, a glass phase forms, and mullitization of the binder occurs. A new phase appears — calcium aluminosilicate $2CaO \cdot Al_2O_3 \cdot SiO_2$, which attests to the interaction in the sample of calcium aluminates with microsilica. The microsilica content determines the structure of the concrete, and initiates mullitization of the binder, which increases the refractory properties of the material as a result of the formation of a mullite phase.

The investigations of the refractory concretes manufacture by the Semiluki Works on the basis of fireclay and an integral binder with VGTs showed that as a result of heat-treatment of the concrete to 380°C dehydration processes are practically completed in the binding material, and with further heating to 1000°C a glass phase is formed and mullitization of the binder occurs. The phase composition of the concrete binder obtained on the basis of highly dispersed silica (microsilica) is similar to that of the binder used in classical fireclay sintered materials.

The investigations show that unsintered concrete articles can be used in thermal equipment for used in glassmaking.

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